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CATALYTIC CRACKING OF DIESEL FUEL FOR ARMY FIELD BURNERS

Part II

Demonstration of Long-Term Performance and Production of a Prototype Catalytic Cracking Unit

by
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13. ABSTRACT (Maximum 200 words) This is one of three reports of a study to develop an advanced fuel conversion process to produce gaseous fuel for field burners. In this process, a gaseous mixture of light hydrocarbons is produced via the catalytic cracking of logistic fuels like diesel and JP-8. This innovative concept leads to a new generation of field burners which are relatively simple, reliable, easy to start and environmentally favorable. This report (Part II) contains results of objectives to demonstrate the long-term performance (durability and reliability) of a catalytic cracking process developed during Phase I and to produce a prototype catalytic burning unit. These objectives were fully met successfully operating a catalytic cracking reactor unit operating on diesel for 300 hours. In addition, a working prototype catalytic burner was successfully developed by slightly modifying an existing M-2 burner unit. By modifying the design and material of the existing M-2 burner vaporizer and using an M-3 burner preheater, we achieved a relatively short preheating time of less than 5 minutes. The first report (Part I, Natick/TR-00/004) was to experimentally demonstrate the feasibility of a catalytic cracking process to produce hydrogen and light hydrogen molecules from diesel with a minimal yield of heavy hydrocarbon residues. A third report (Part III, Natick/TR-00/006) discusses results of the objective to develop a centralized fuel-processing unit for large-scale multiburner operation utilizing the catalytic cracking technology.			
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Preface

The study reported here was conducted under U.S. Army Soldier and Biological Chemical Command (SBCCOM), Soldier Systems Center, contract No. DAAK60-94-C-0030. The work was performed by Hamed Borhanian, Jae Ryu, and Alan Zhou of Aspen Systems, Inc., Marlborough, MA. Mr. Donald Pickard of the Soldier Systems Center was the project officer for the contract.

This report is one of a series of three. The references for the other reports are:

Ryu, J., (1994). *Catalytic Cracking of Diesel Fuel for Army Field Burners. Part I: Feasibility of Producing Gaseous Fuel from Diesel Fuel via a Catalytic Cracking Process*, (Tech. Rep. NATICK/TR-00/004). Natick, MA: Soldier Systems Center, U.S. Army Soldier and Biological Chemical Command (SBCCOM).

Borhanian, H., Zhou, A., (1998). *Catalytic Cracking of Diesel Fuel for Army Field Burners, Part III: Study of Catalytic Cracking and Steam Reforming* (Tech. Rep. NATICK/TR-00/006). Natick, MA: Soldier Systems Center, U.S. Army Soldier and Biological Chemical Command (SBCCOM).

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CATALYTIC CRACKING OF DIESEL FUEL FOR ARMY BURNERS

PART II

Demonstration of Long Term Performance and Development of a Prototype Catalytic Cracking Burner Unit

Executive Summary

The overall objective of this program was to develop an advanced fuel conversion process to produce gaseous fuel from diesel for field burners. In this process, a gaseous mixture of light hydrocarbon molecules was produced via catalytic cracking of diesel. This innovative concept allows for the development of field burners which are relatively simple, reliable, and easy to start. Furthermore, the gaseous light hydrocarbons promote clean combustion, which is environmentally favorable.

The objectives of Phase II of this three-phase program were to demonstrate the long term performance (durability and reliability) of a catalytic cracking process developed during Phase I and to produce a prototype catalytic cracking burner unit. In Phase II, we fully met these objectives by successfully operating a catalytic cracking reactor unit operating on diesel for 300 hours. Clean combustion (blue flame) of diesel was clearly demonstrated during the entire test period of 300 hours. There was no sign of coking or sulfur poisoning of the catalysts during this experiment. In addition, a working prototype catalytic cracking burner was successfully developed by slightly modifying an existing M-2 burner unit. By modifying the design and material of the existing M-2 burner vaporizer and using an M-3 burner preheater, we achieved a relatively short preheating time of less than 5 minutes.

In addition, several prototype catalytic cracking reactor units (vaporizer) were fabricated and delivered to Army Natick RD&E Center. Multifuel capability of the catalytic cracking burner system was successfully demonstrated by operating this burner with blue flame on Exxon No. 2 diesel (0.025% sulfur), Army No. 2 diesel (maximum 0.5% sulfur), JP-8, and gasoline.

In Phase III Aspen will develop a centralized fuel-processing unit for large-scale multi-burner operation utilizing the catalytic cracking technology. Aspen will design and fabricate a self-powered, centralized fuel processing and field burner unit utilizing a thermoelectric power generation technology. As an option, a fuel-based, electric power generation unit will be investigated for "more-electric-powered" field kitchen systems.

When successfully developed, the proposed concept will have tremendous potential for a wide range of residential and commercial applications. For example, residential gas appliances (i.e., heating systems, stoves, grills, and clothes dryers) could be operated by the gaseous fuel produced from the fuel processing units. The benefits of this application will include increased energy efficiency and clean oil combustion, the reduction of the length of gas transport lines, and reduced risks associated with handling gaseous fuel. Similar advantages could be realized for commercial applications.

1. Phase II Technical Objectives

The primary goal of this three-phase program was to design and fabricate a catalytic cracking unit to retrofit current Army vaporizing field burners. All the necessary components in the current field burner system (M-2) were to be modified and optimized accordingly, and the reliability and durability of the prototype catalytic cracking/burner unit were to be demonstrated by conducting long term performance tests on diesel fuel. The specific objectives were:

- To design and fabricate a prototype fuel processing unit to retrofit into an existing Army field burner;
- To demonstrate the reliability and durability of the proposed catalytic cracking fuel processing unit/burner combination by evaluating its performance during 300 hours of operation; and
- To demonstrate the multifuel capability by successfully operating a prototype unit using kerosene and lower grade diesel fuels.

The achievements realized during Phase II (December 27, 1994 - August 14, 1995) are discussed in the following sections.

2. Introduction

2.1. Background

Cracking of heavy hydrocarbons to produce light hydrocarbons has been practiced for almost two hundred years, and may be classified into two categories: thermal cracking and catalytic cracking. Thermal cracking involves many chemical reactions, including dehydrogenation, polymerization, and isomerization. However, the primary chemical reaction involves the formation of free radicals by the random loss of hydrogen atoms to other free radicals, followed by a carbon chain rupture to the hydrogen deficient carbon atom. Thus, many different carbon chain lengths are possible in the final product as a result of thermal cracking.

The use of catalysts to modify the yields and quality of cracked products was initiated as early as 1915 and was successfully commercialized in the 1930's. Since then, major efforts have been focused on the development of highly efficient catalysts and economical cracking processes⁽¹⁻⁴⁾ to increase the yields of valuable products, such as high octane gasoline for the petroleum industry. In parallel, there has been a continued effort to produce synthetic fuel from coal utilizing the catalytic cracking process. Both syngas and liquid fuels have been commercially produced via catalytic cracking of tar.⁽⁵⁻⁸⁾ The exact mechanism involved in catalytic cracking of hydrocarbons is not precisely known, although a staggering amount of research has been published on the effects of catalysts, operational variables, and feedstock quality on product yields.

When cracking occurs, there is a hydrogen deficiency in the reaction, and complex reactions follow to reconcile the unsaturated light hydrocarbons (light olefins). Reactions that may occur include polymerization, formation of aromatic hydrocarbons, and coking. Most of these secondary reactions of light olefins are undesirable and reduce the yield of gaseous products. The degree of these secondary reactions, which will determine the product distribution in the cracking process, depends heavily upon process conditions. Furthermore, the addition of various cracking promoters or product stabilizers, such as water, air, or hydrogen (recycled from the product stream), can significantly suppress the above-mentioned secondary reactions. However, supplying water to the fuel conversion process may be logically unfavorable for certain Army field operations, and air injection or recycling hydrogen product may require a power source.

As mentioned above, catalytic cracking of heavy hydrocarbons to produce light hydrocarbons is a well established process in the petroleum and coal industries. However, the specific process of catalytic cracking of diesel to produce light hydrocarbons has not yet been investigated. There have been intensive but less than fruitful research efforts within the U.S. military to produce hydrogen via reforming of diesel. The purpose of these programs was to provide electricity utilizing phosphoric acid fuel cell (PAFC) technology at remote sites.^(9,10) As a result of these efforts, various reforming processes have been successfully developed to produce hydrogen-containing gas mixtures from diesel through slight modifications to well-developed industrial processes.

Independently, there has been a worldwide effort to develop an onboard fuel processing unit for the production of gaseous fuels from liquid hydrocarbons in order to minimize air pollution from internal combustion engines for automobiles.⁽¹¹⁾ For this application, the gaseous product was typically comprised of mostly hydrogen with a small amount of hydrocarbon impurity. As a result of this program, advanced catalysts and catalytic cracking processes were successfully developed. However, for the internal combustion engine, the requirements in fuel product distribution were rather stringent, and, therefore, the onboard fuel processor for automobiles has not yet been realized. Currently, worldwide concerns for a clean environment have re-ignited the interest in the development of onboard fuel processors for the production of zero emission vehicles.

2.2. Catalytic Cracking of Diesel

During Phase I of this program (March 23 - November 23, 1994), Aspen Systems successfully demonstrated the feasibility of producing gaseous fuel from diesel via a catalytic cracking process.⁽¹²⁾ Both the clean combustion of diesel and wide ranges of firing rate controllability were clearly demonstrated using the M-3 burner head. The total energy required to crack one gallon of diesel fuel was determined to be 730 Btu and 680 Btu (with and without the heat loss incurred during the operation, respectively), which is less than the energy required for the vaporization of diesel (theoretical value of 781 Btu/gallon).

The main thrust of Phase II was to develop a prototype cracking unit and retrofit it to current Army field burners. During Phase II (December 27, 1994 - August 14, 1995), Aspen

Systems successfully produced a catalytic cracking reactor unit utilizing the vaporizer of the M-2 burner. We also successfully completed a 300 hour durability test. In addition, we modified the material and design of the existing M-2 burner vaporizer to reduce start-up time. In the following sections, results of the experiments conducted during Phase II will be presented and discussed.

3. Results and Discussions

3.1. Retrofit Current Burner System for 300-Hour Demonstration

Vaporizer (catalytic cracking reactor) Modification

The main thrust of Phase II was to produce a reliable prototype fuel processing unit to be retrofitted into an existing Army vaporizing field burner (M-2), and to demonstrate the reliability and durability of the catalytic cracking/burner unit by conducting long term performance tests on diesel fuel. For this demonstration, we modified the vaporizer of an M-2 burner into a catalytic cracking reactor as shown in Fig. 1. The body of the M-2 burner vaporizer itself was not changed, but the fuel feed side of the vaporizer was cut and opened, and a metal seal flange was welded onto it. As a result of this modification, the vaporizer could be used as a holding vessel for the catalysts (catalytic cracking reactor), whose content could be easily replaced. In addition, a type K thermocouple was inserted into the middle of the catalytic cracking reactor to monitor the catalyst bed temperature at the pre-heating stage and during burner operation. About 475 gr (1.05 lbs) of catalysts was packed into the M-2 burner vaporizer which was secured using thin stainless steel screens and 1.5" thick ceramic wool plugs at both ends. Pictures of the original M-2 burner vaporizer and the modified vaporizer (the catalytic cracking reactor), complete with catalysts and embeded thermocouple, are shown in Fig. 2.

In addition, the nozzle part of the vaporizer was insulated by wrapping it with ceramic strips insulation (2" wide and 1/8" thick, McMaster-Carr No. 87575K88) in order to prevent the cooling and condensing of gaseous fuel from the vaporizer. During the catalytic cracking burner operation, we noticed that the maximum firing rate of the burner was limited by the area of the opening allowed for the existing air inlet. For example, when the burner firing rate was greater than about 50,000 Btu/hr, the burner flame became too rich (yellowish) because of a lack of either oxygen or air. Therefore, we increased the size of the air inlet openings of the existing burner (6 trapezoid-shaped openings) from 1.125 inch² to 2.65 inch² each. After increasing the size of the air inlet, we could operate the burner at high firing rates (greater than 60,000 Btu/hr) while maintaining a blue flame.

Catalytic Cracking Burner Operating Procedures

After installing the catalytic cracking reactor (modified vaporizer) to the M-2 burner unit, we began heating it via a MAPP (Methyl Acetylene-Propadiene) gas-air torch. The diesel fuel was introduced into the catalytic cracking reactor when the catalyst temperature reached about 250°C (482°F) by pressurizing the fuel tank. During this stage, the nozzle remained closed. Once the catalyst temperature reached 300°C (572°F), the nozzle was slowly opened and fuel was introduced into a mixing chamber and lit at the flame holder. During normal operation, it took

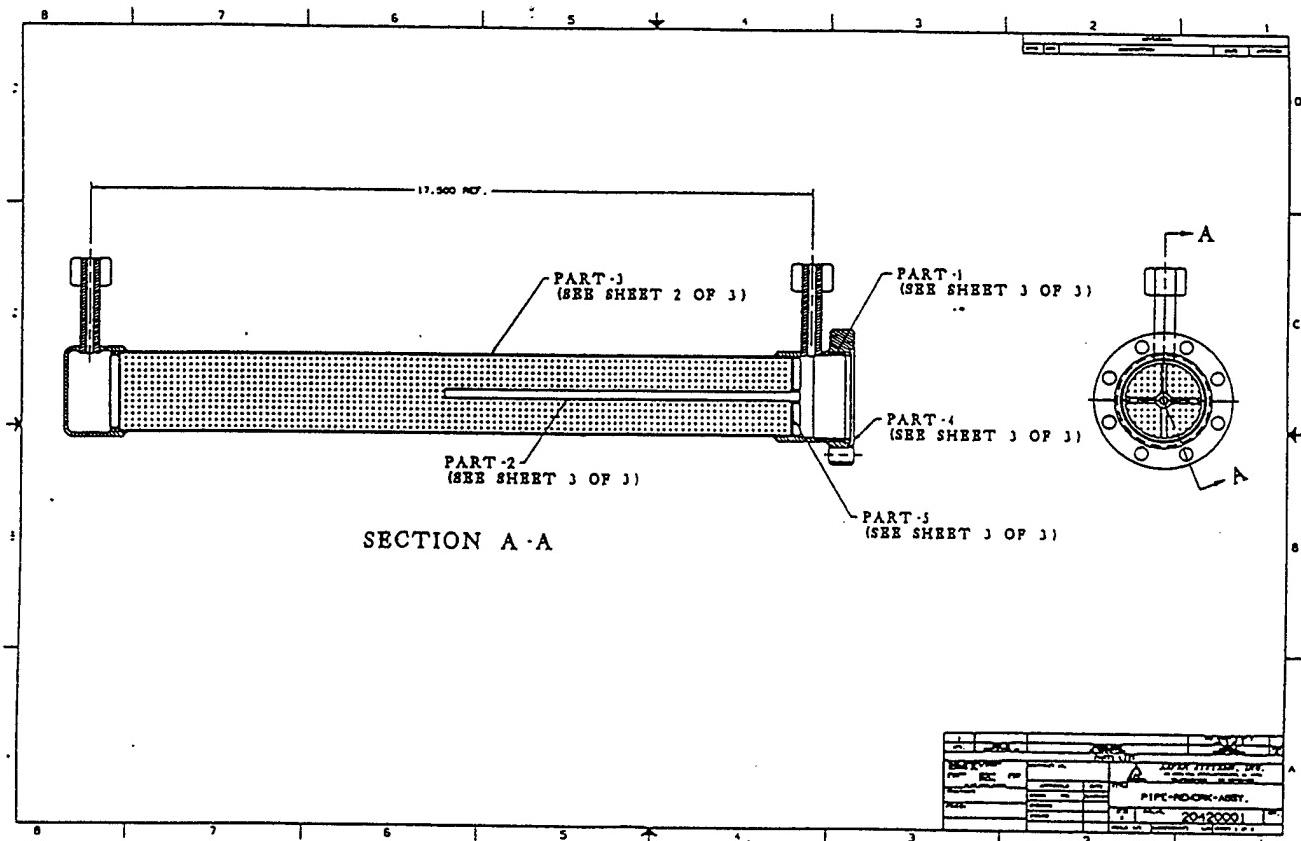


Figure 1: Schematic of the First Version of the Catalytic Cracking Reactor (Modified Vaporizer) Used on the M-2 Burner Unit.

about 20-30 minutes to complete the preheating of the 475 gr (1.05 lbs) of catalyst in the steel vaporizer tube (M-2 burner vaporizer). Minimization of start-up time (the time required for the preheating of the catalyst bed) is an important issue for Army field burner operation. We were able to reduce the start-up time to less than 5 minutes by using a different catalytic cracking reactor (vaporizer) tube material. Detailed results will be presented in a later section.

At the burner's start, the temperature of the catalyst bed always decreased as cold fuel was introduced into the catalytic cracking reactor. For example, the catalyst bed temperature decreased to 250°C (482°F) - 270°C (518°F), depending upon the rate of cold fuel being fed into the cracking reactor (vaporizer) and the flame temperature. Under optimal operating conditions, the catalyst bed temperature stabilized within 1-2 minutes after start-up, and the catalyst bed temperature remained above 270°C (518°F). When the catalyst bed temperature decreased below 250°C (482°F), diesel to gaseous fuel conversion via the catalytic cracking was very low. In this case, the dripping of uncracked diesel fuel was severe, burner flame became completely yellow, and the catalyst bed temperature continuously decreased. Once this happened, the nozzle had to be closed (in order to stop introducing fuel into the catalytic cracking reactor) and the preheating step had to be restarted.

For the 300 hour demonstration, we used Exxon No. 2 diesel fuel obtained from a local Exxon gas station. Specifications of this fuel are listed in **Table 1**. In addition, we used a compressed air cylinder to pressurize the fuel tank. Typically, the air delivery pressure was set at 22 psi, which provided a fuel tank pressure of around 18-20 psi. In normal operation, the catalyst bed temperature was always between 270°C (518°F) and 300°C (572°F).

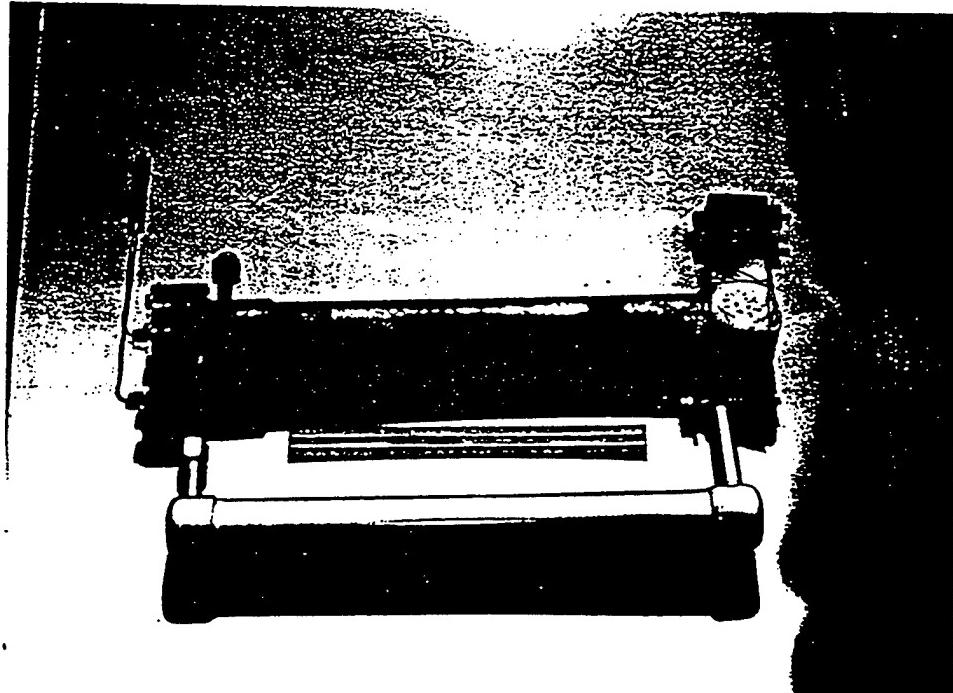


Figure 2: Picture of the Catalytic Cracking Reactor (Modified Vaporizer).

Table 1: Specifications of the Commercial Diesel Fuel (Exxon No. 2-D) Used for the 300 Hour Demonstration.¹

Cetane Number	40
Flash Point, °C (°F)	52 (125)
Water and Sediments, % vol	0.05
Distillation Temperature (90% vol. recovered), °C (°F)	338 (640)
Kinematic Viscosity, mm ² /sec at 40°C	1.9 - 4.1
Density, kg/m ³ (lb/gallon)	876 (7.32)
Ash %	0.01
Sulfur % ²	0.025

1: Specifications provided by Exxon

2: Actual sulfur content in the diesel fuel. Determined by using ASTM D4294-83, X-Ray Fluorescence Spectrometry with detection limit of 0.01%

3.2. Long Term Performance Demonstration

One of the main objectives of Phase II was to demonstrate the durability of the catalytic cracking process for Army field burners operating on diesel. In order to demonstrate the durability of the catalytic cracking technology, we operated the catalytic cracking burner on diesel for 300 hours. Details of the procedures and results of this experiment are presented in detail in this section.

300-Hour Demonstration

Generally, coking and/or sulfur poisoning of the catalysts are great concerns during the process of the catalytic cracking of hydrocarbons containing sulfur. The modified M-2 catalytic cracking burner was operated on diesel for 300 hours following the procedures described in the previous section. Burner performance, such as blue flame combustion, fuel consumption (firing) rate, catalyst bed temperature, and fuel tank pressure, was carefully monitored and recorded during the operation. The firing rate was determined by measuring the burner weight change (or fuel consumed) for a given period of burner operation. For example, as shown in Fig. 3, the total weight of the burner was 63 lbs. with a full tank of diesel. The full tank of diesel was completely consumed after 7.4 hours of burner operation, and the burner weight was reduced to 40 lbs. Therefore, we consumed 23 lbs. of diesel (446,200 Btu) in 7.4 hours, which corresponds to a firing rate of 60,297 Btu/hr.

This experiment began on March 7, 1995 and lasted until May 12, 1995. Each working day we operated the catalytic cracking burner for 6-8 hours and consumed about 21-23 lbs. of diesel per day. We consumed a total of about 132 gallons (966.26 lbs.) of diesel during the 300

hour operation, which corresponds to 3.22 lb/hr (62,484 Btu/hr) of diesel consumption. During this period, we did not notice any degradation of the catalytic cracking unit, as is clearly shown in Fig. 4 by the constant slope in the fuel consumption rate. Since we always operated the burner with blue flame, the constant slope in the fuel consumption rate (or firing rate) indicated a consistently excellent performance by the catalytic cracking unit during the 300 hour operation.

The temperature of the catalytic cracking unit was normally in the range of 270°C (518°F)-300°C (572°F) during the 300 hour operation, as depicted in Fig. 5. Most of the time the temperature was self-regulated within this temperature range. However, occasionally the catalyst temperature either slipped down below 260°C (500°F) or climbed up to 320°C (608°F), depending upon the external conditions such as any existing wind around the burner operation area. In either case, we were able to maintain a blue flame in the burner by slightly adjusting the fuel control (nozzle) or air valves. During this period, we also investigated the effect of placing a cooking pot (filled with water) on top of the burner. The result of this experiment indicated that the vaporizer temperature increased about 10-20°C (50-60°F). We believed that the presence of the water pot prevented the heat from escaping from around the vaporizer area.

During the 300-hour demonstration experiment, Aspen used a compressed air cylinder to pressurize the fuel tank for fuel feed. Air delivery pressure from the gas cylinder to the fuel tank was approximately 22 psi during the 300 hour operation. As shown in Fig. 6, the fuel tank pressure fluctuated slightly between 18-20 psi. While the reason for the slight fluctuation of the fuel tank pressure was not clear, it did not affect the performance of the catalytic cracking burner.

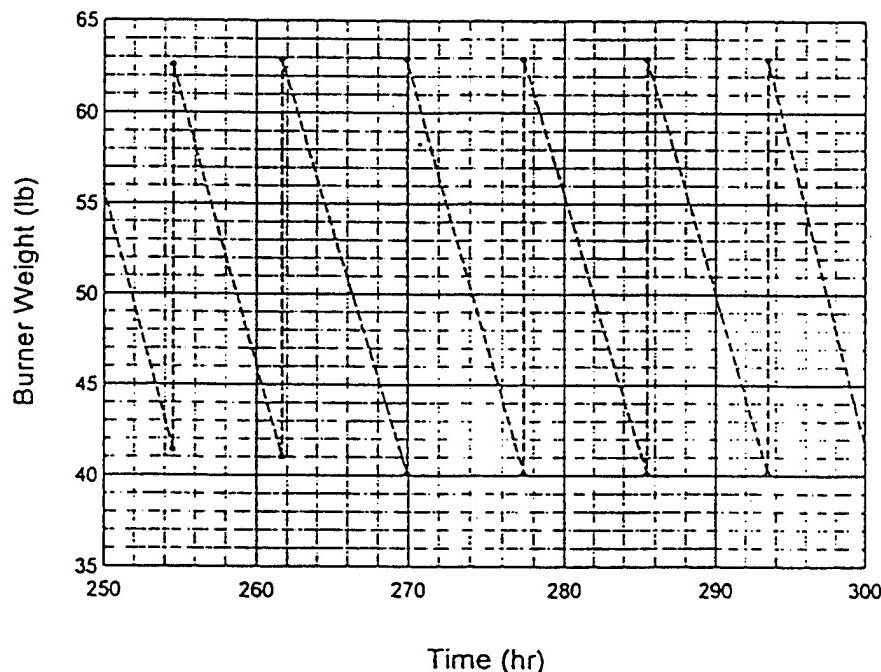


Figure 3: Changes in Weight of the Catalytic Cracking Burner Unit During the 300 Hour Operation. Burner Weighed Around 63 lbs. with Full Tank of Diesel and Weighed Around 40 lbs. When the Fuel Tank Was Empty.

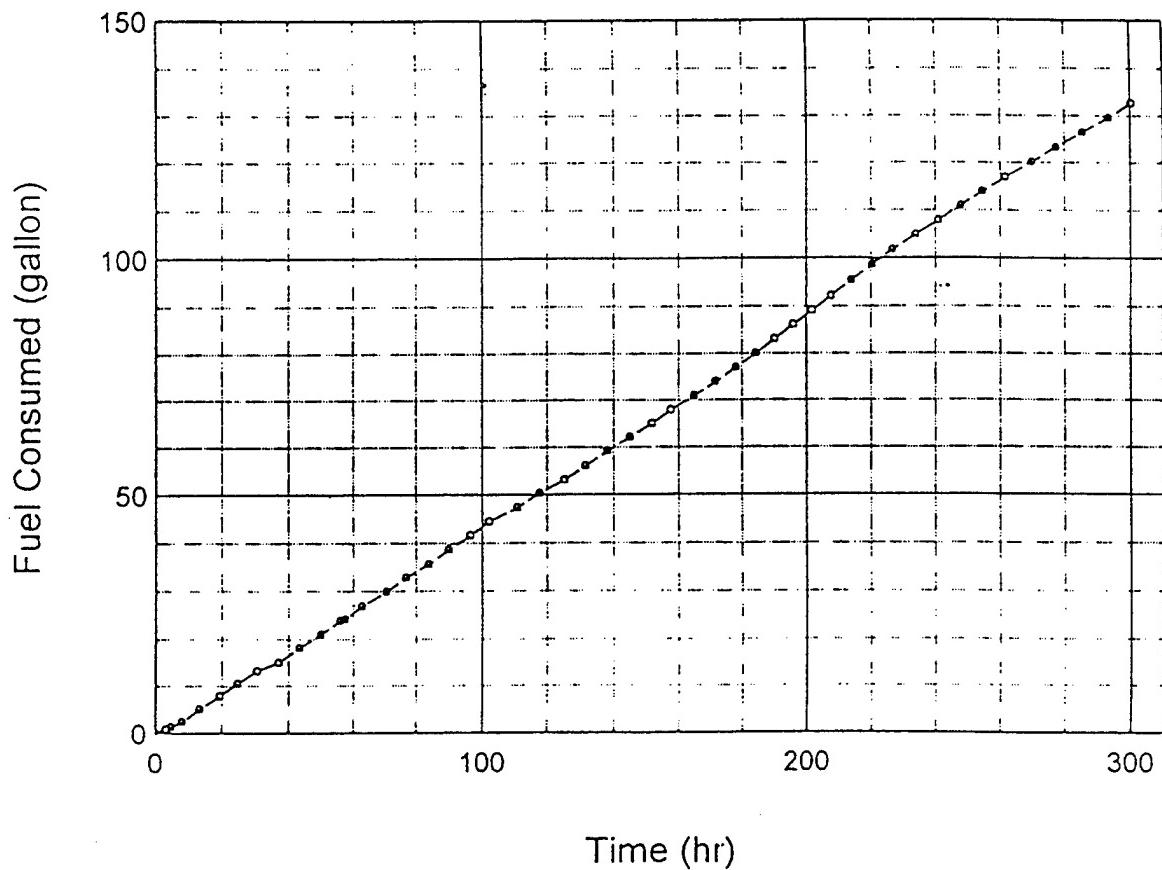


Figure 4. Amount of Diesel Fuel Consumed During the 300-Hour Operation
Constant Slope in Fuel Consumption Indicates the Consistency in
Burner Performance.

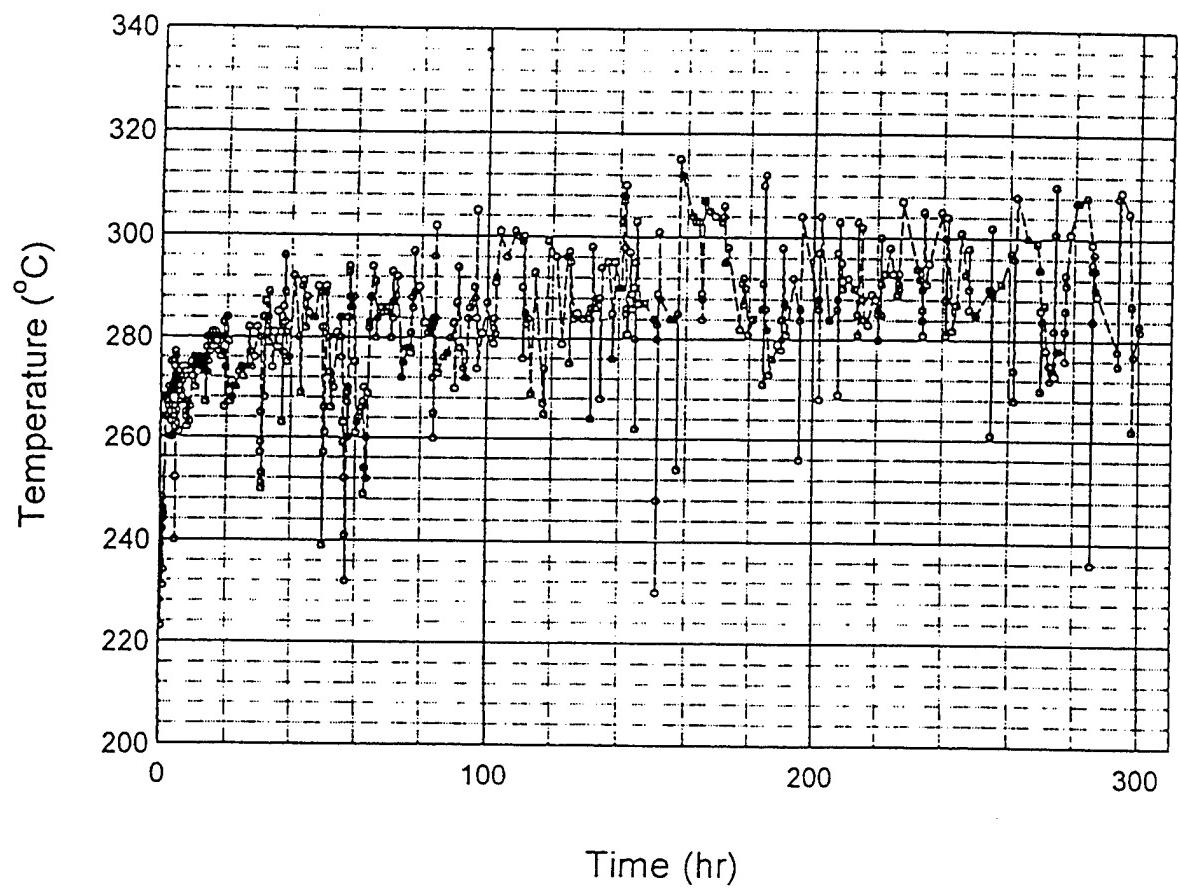


Figure 5: Temperature of the Catalytic Cracking Unit (Vaporizer) During the 300-Hour Operation.

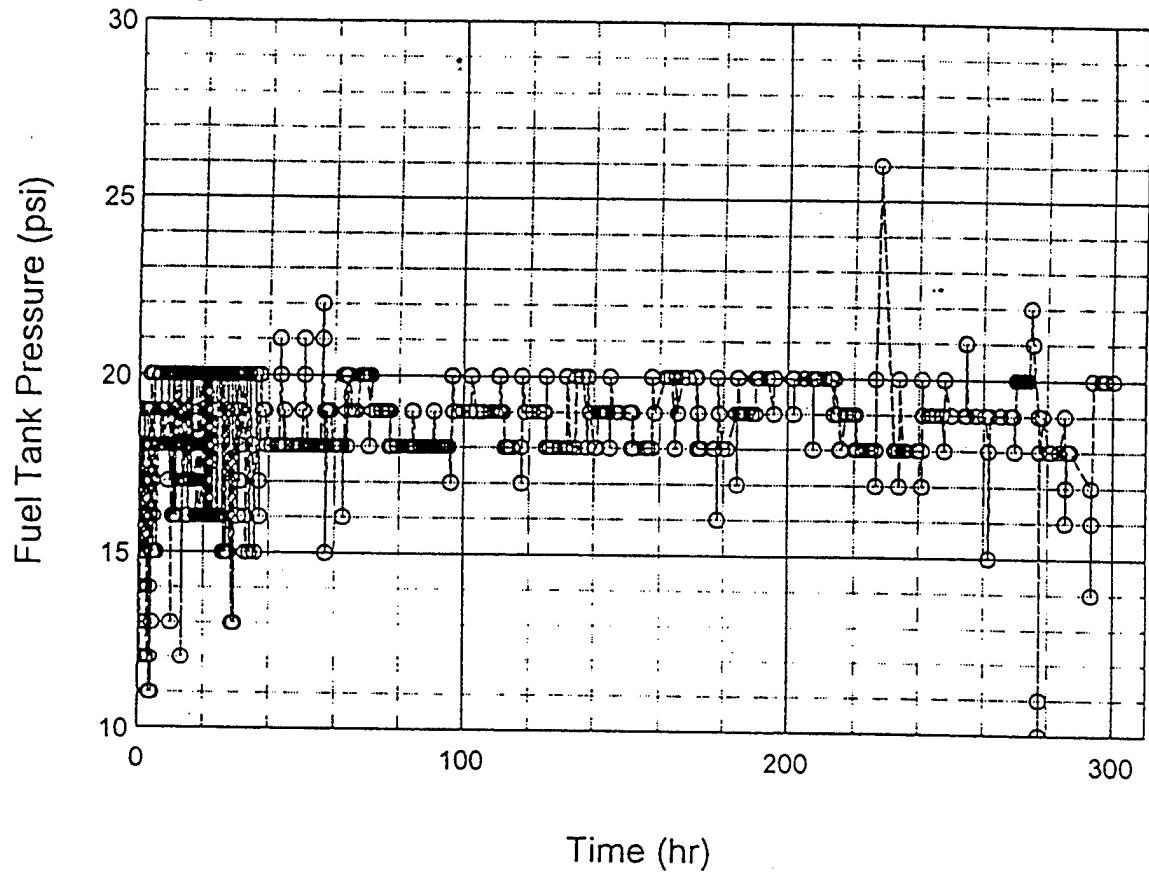


Figure 6: Fuel Tank Pressure of the Catalytic Cracking Burner Unit During the 300-Hour Operation.

In summary, we successfully demonstrated the durability of the catalytic cracking process for Army field burner operation. There was no degradation of catalyst performance during the 300-hour operation, as is proven by the consistent blue flame combustion of diesel.

Catalyst Poisoning Evaluation

Catalyst poisoning is a serious problem for any reaction process utilizing catalysts. There are two potential sources of catalyst poisoning that could occur in the process of the catalytic cracking of diesel: sulfur poisoning and coking. Sulfur poisoning generally occurs in two ways: corrosion of the catalyst support by the acidic sulfur compounds and/or deactivation of the catalyst via covering the active sites of the catalysts with solid or liquid phase sulfur. Coking also results in the deactivation of the catalyst via covering the active sites of the catalysts with solid carbon.

After the 300-hour operation, the catalysts were carefully removed from the catalytic cracking unit (vaporizer) for visual inspection and chemical analyses. A picture of the catalysts removed from the vaporizer after the 300-hour operation is shown in Fig. 7. As shown in this picture, catalysts located within 2-3 inches of the fuel supply side were slightly darker in color than those taken from other areas. Aspen believed that the low temperature of these catalysts, due to the continuous cooling of the catalysts by the cold fuel, caused the different appearance of the catalysts in this area. Upon visual inspection, we were unable to notice any signs of significant coking or sulfur accumulation in the catalysts.

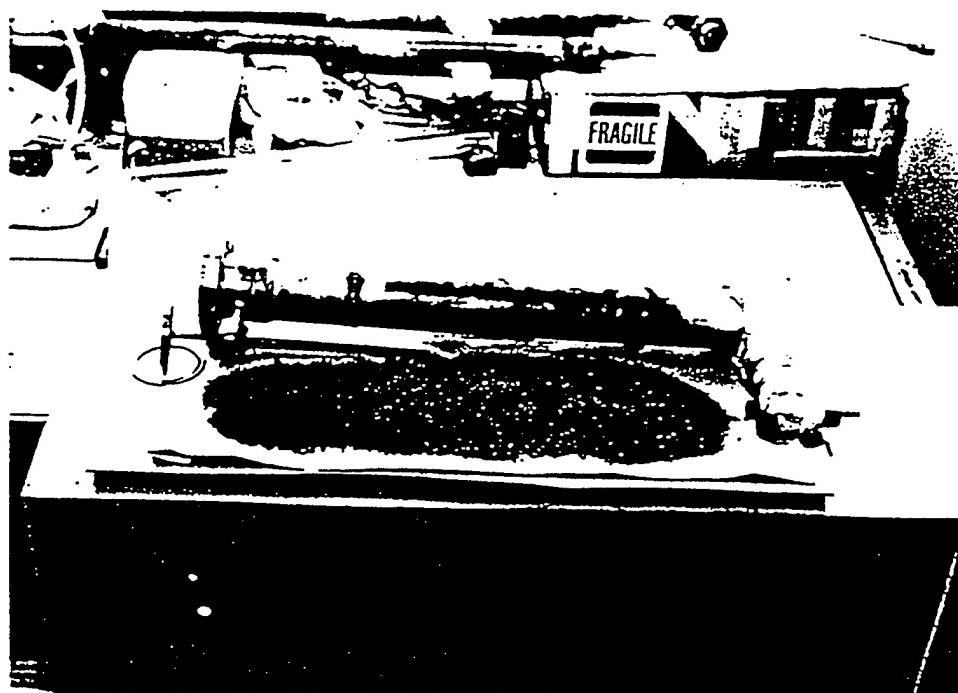


Figure 7: Picture of the Catalysts and the Vaporizer Tube
After 300-Hours of Operation on Diesel.

In the catalytic cracking process, fuel-bound sulfur in the diesel fuel may be carried away from the vaporizer by the gaseous fuels or accumulated in the catalysts in the form of liquid or solid sulfur. In order to determine the location of the sulfur in the diesel fuel, we analyzed the sulfur content in the catalysts after the 300 hour operation. For this analysis, catalysts from various parts of the vaporizer, as shown in Fig. 8, were collected and lightly washed with ethanol to remove any diesel fuel left in the catalysts. An ASTM method D 4294-83 (X-Ray fluorescence spectrometry) with a detection limit of 0.01% was employed for sulfur analysis. The results of this analysis are summarized in Table 2. The sulfur content in the diesel fuel was 0.025%, whereas the content in the catalysts at the fuel inlet side (relatively dark colored chunks) was 0.066%. Catalysts collected within 2-3 inches from the fuel inlet contained about 0.026% of sulfur. However, sulfur was not detected from the catalysts collected at either the middle or nozzle side of the vaporizer. This result implied that sulfur poisoning did not occur in the catalytic cracking process.

3.3. Prototype Catalytic Cracking/Burner Unit Development

As discussed in the previous section, catalytic cracking technology is a remarkably reliable means of promoting the clean combustion of diesel fuel. However, initially, a relatively long time was required to preheat the catalytic cracking reactor to an elevated temperature. Typically, it took 25-30 minutes and 12-15 minutes to heat a modified M-2 burner vaporizer to 300°C (572°F) using a MAPP gas-air torch and an M-3 burner preheater, respectively. Since these preheating

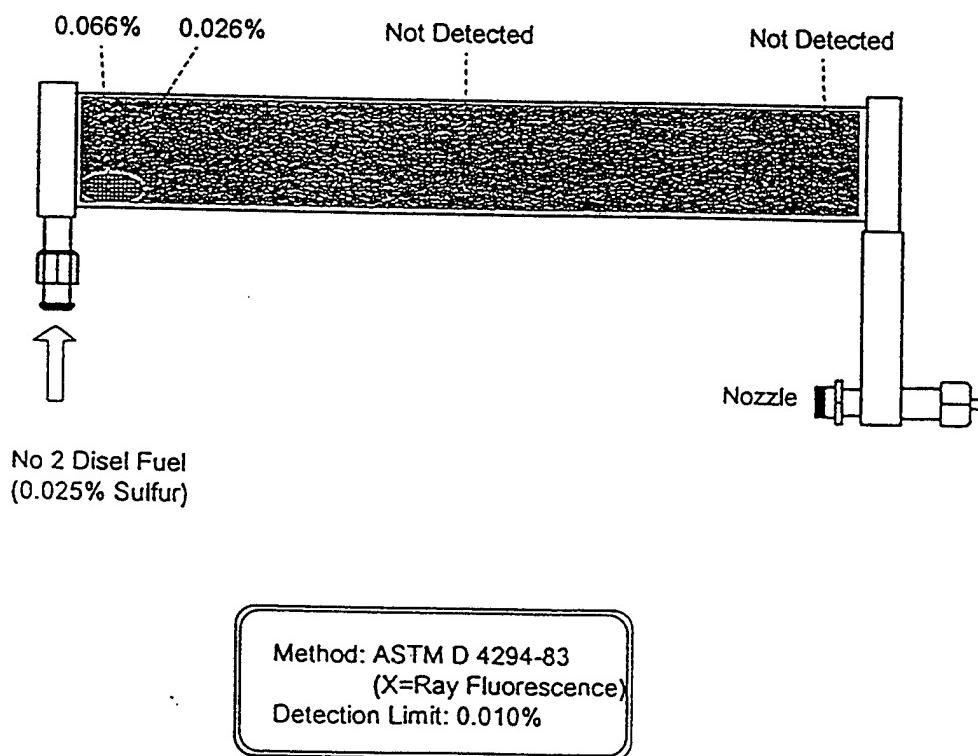


Figure 8: Location of the Samples Collected for Sulfur Content Analysis and Their Sulfur Contents After the 300-Hour Operation.

Table 2.: Sulfur Content in the Catalysts After the 300 Hour Operation.¹

Location of the Sample Collected	Sulfur Content (Weight %)
No. 2 Diesel Fuel (commercial)	0.025
Catalysts from the nozzle side of the vaporizer	Not detected
Catalysts from the middle of the vaporizer	Not detected
Catalysts from the fuel inlet side of the vaporizer	0.026
Chunk of dark colored catalysts at the fuel inlet	0.066

1: Determined by employing ASTM D4294-83 (X-Ray Fluorescence Spectrometry) with the detection limit of 0.010%

were very likely not acceptable for the Army's field operation, we further modified the catalytic cracking M-2 burner unit to reduce the preheating time. This modification work included:

- Using high thermal conductivity vaporizer tube material and small diameter tube;
- Installing M-3 burner preheater on the catalytic cracking M-2 burner unit; and
- Modifying an existing preheater shield to cover the entire length of the catalytic cracking reactor (vaporizer) tube.

Optimization of the Catalytic Cracking Reactor Tube

The original vaporizer tube was made of alloy steel with a 1.994" OD and a length of 16.5". We believed that the preheating time could be significantly shortened by using high thermal conductivity vaporizer tube material and by reducing the diameter of the tube.

As shown in Table 3, the thermal conductivity of alloy steels is an order of magnitude smaller than that of copper. However, alloy steel is cheap, relatively chemically inert, and exhibits relatively high mechanical strength at elevated temperatures. Copper exhibits the highest thermal conductivity among all candidate materials, and many different sizes of copper tubes are readily available. However, its mechanical strength is low and it is chemically reactive to sulfur-containing fuel vapors. Other copper alloys and pure nickel tubes offer moderate values of thermal conductivity and mechanical strength at elevated temperatures. However, these materials are not readily available in small quantities.

For this program, we decided to use copper tube as the catalytic cracking reactor (vaporizer) tube material because of its extremely high thermal conductivity. The chemical reaction of the copper with the sulfur-containing compounds at elevated temperatures can be effectively minimized by coating a thin layer of nickel on the copper. A local electroless plating company was identified and it was determined that they could provide thin nickel coating (about 1-2 mil thick) on copper at a reasonable price. Before making a final decision, we tested the

Table 3. Thermomechanical Properties of the Candidate Materials for Catalytic Cracking reactor Tube.

Materials	Thermal Conductivity, W/mK at Temperature (°C)	Yield Stress ⁽¹⁾ , MPa at Temperature (°C)
Low alloy steel	30-50 (R.T.)	300-400 (R.T.)
	30-40 (400)	250-400 (400)
18-8 stainless steel	16 (R.T.)	234 (R.T.)
	20 (400)	93 (600)
O.F.H.C. copper	399 (R.T.)	78 (R.T.), 70 (204)
Beryllium copper	100-200 (R.T.)	200-600 (R.T.)
Bronze (70/30)	121 (R.T.)	97 (R.T.), 88 (300)
Brass (60/40)	126 (R.T.)	96 (R.T.), 105 (204)
Nickel	75 (R.T.)	170 (R.T.), 140 (400)
Monel 400	22 (R.T.)	230 (R.T.), 220 (400)
Inconel 600	15 (R.T.)	250 (R.T.), 185 (400)

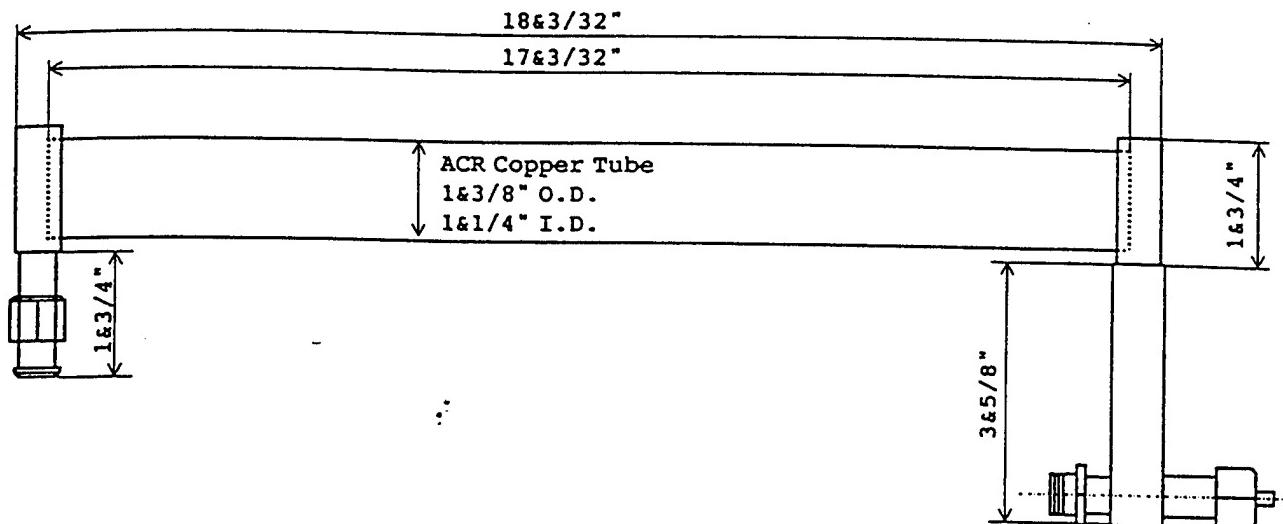
1: Yield stress of the soft material, such as copper, are 0.2% offset proof stress.

mechanical strength of the copper tube at elevated temperatures. For this test, we purchased 1 3/8" OD and 1 1/4" ID copper tubing (ACR grade, 0.0625" wall thickness). Upon heating the tube to 500°C (932°F), the tube was pressure tested up to 40 psi using compressed helium. The result of this experiment indicated that the mechanical strength of the copper tube was high enough to be used as a vaporizer tube material for the Army burner when normal operating conditions were less than 20 psi of pressure at 300°C (572°F).

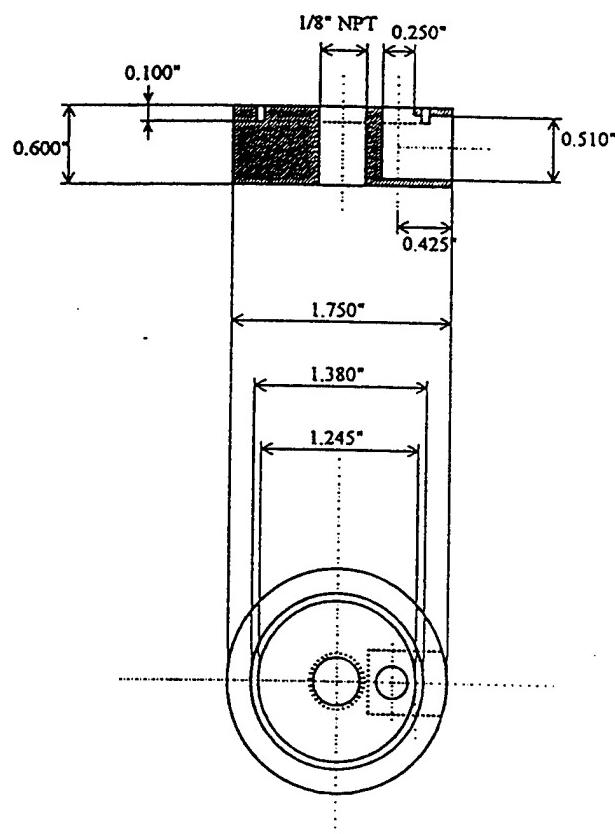
Upon the successful completion of the mechanical strength tests of the copper tube, the modified vaporizer (catalytic cracking reactor) unit was designed and fabricated. A schematic of this unit is shown Fig. 9. The catalytic cracking reactor tube and both side end caps were made of copper. Machined copper components were electroless coated with nickel (1 mil thick) both inside and outside to protect the copper from reacting with fuel vapor. The feed tube and flame valve (nozzle) tube were removed from the M-2 burner vaporizer and used. Pictures of the modified catalytic cracking reactor installed in the M-2 burner unit and its blue flame combustion are shown in Fig. 10 and Fig. 11. The amount of catalysts used in this small diameter (1 1/4 ID) reactor tube was 215 gr (0.47 lbs).

Modification of Preheater Configuration

The existing M-2 burner preheater was designed for operating on gasoline and for preheating the nozzle side of the vaporizer tube. Since the catalytic cracking burner will be operating on diesel, we had to use a different type of preheater and a different configuration.



Feed Side End Plate



Nozzle Side End Plate

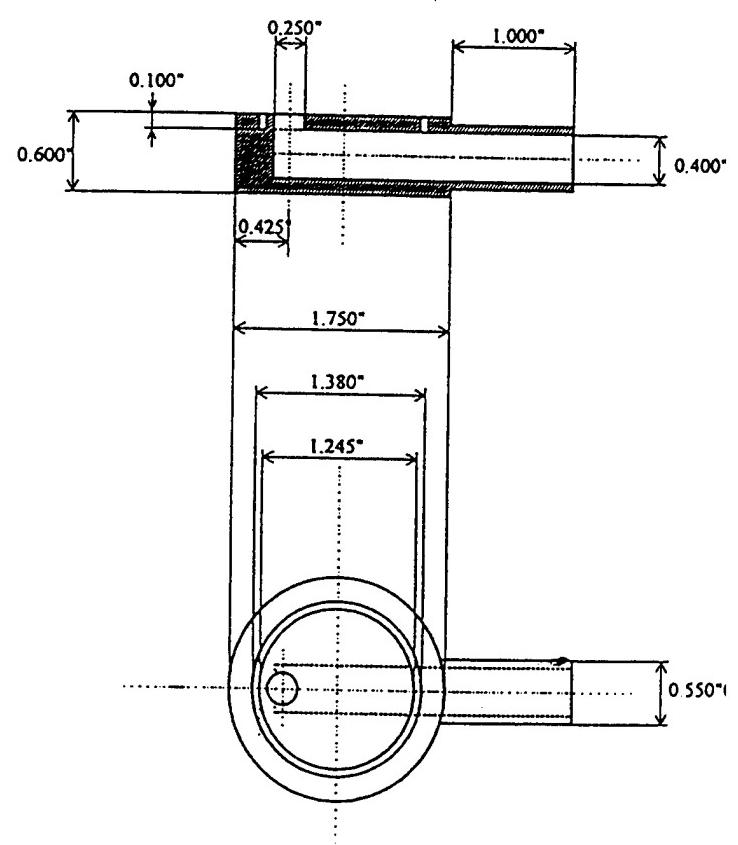
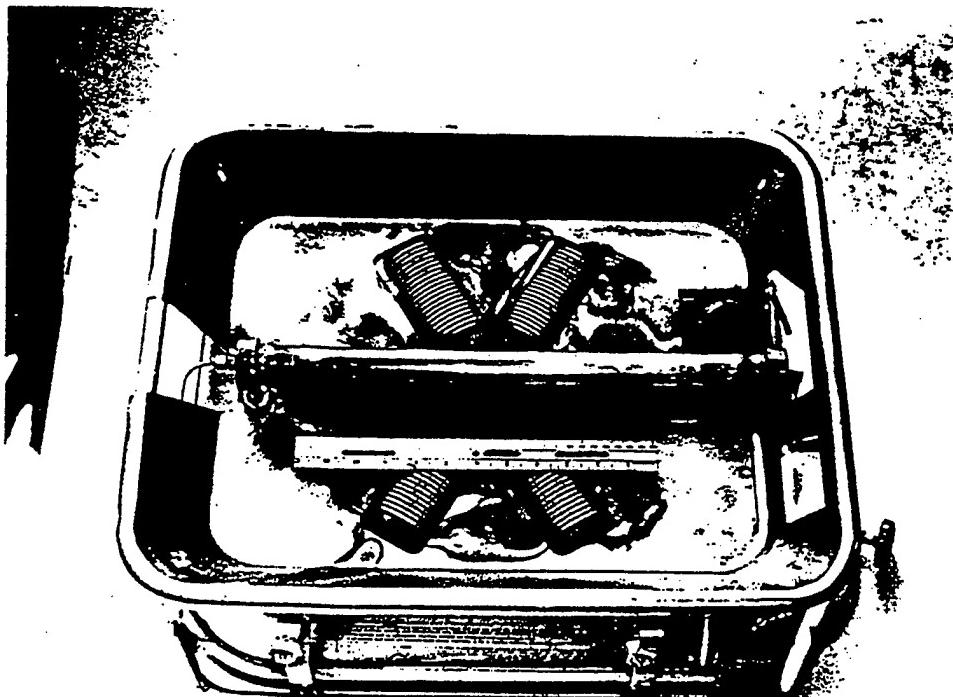


Figure 9: Schematic of the Modified Catalytic Cracking Vaporizer Made of Copper Tubing and End Caps. All These Components Were Electroless Nickel Plated.



**Figure 10: Picture of the Modified Catalytic Cracking Vaporizer
Mounted on an M-2 Burner Unit.**

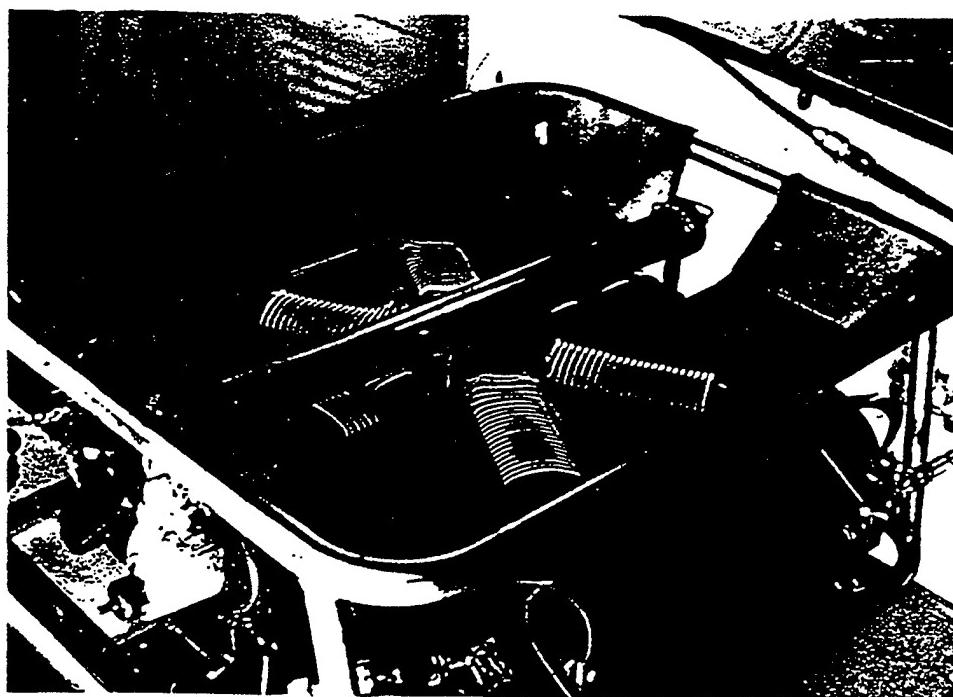


Figure 11: Blue Flame Performance of the Prototype Catalytic Cracking Burner Unit.

Fortunately, the specifications of the M-3 burner preheater match quite well with the preheater requirements of our application. Therefore, we used the M-3 burner preheater without any modifications for this program. For the development of the prototype catalytic cracking burner unit, we installed the M-3 burner preheater into an M-2 burner fuel tank by slightly modifying the fittings and air/fuel feedlines. A schematic of the preheater installed in the prototype catalytic cracking burner unit is shown in Fig. 12.

In order to further reduce the preheating time by preserving the heat around the catalytic cracking reactor during preheating, we fabricated and installed a heat shield on top of the catalytic vaporizer tube. The preheating time needed to reach the operating temperature in the catalytic cracking reactor, with the modified vaporizer tube and the M-3 burner preheater, was about 4-5 minutes. We also investigated the effect of the adding copper chips to the catalysts on the preheating time required. By mixing the high thermal conductivity copper chip with the catalysts, thermal conduction through the catalysts can be significantly enhanced. In this program, we mixed about a 30% volume of copper chips with the catalysts and filled a larger diameter reactor tube (2" ID) with the mixture. Although we did not notice a significant improvement (reduction) in preheating time, we found several beneficial effects by the addition of the copper chips. These effects included: (1) a significant decrease in the amount of liquid dripping at the nozzle during burner startup; and (2) ease of stabilization of the catalyst temperature at the early stage of the burner operation.

3.4. Multifuel Capability Demonstration

One of the objectives of the Phase II program was to demonstrate the multifuel capability of the catalytic cracking burner. After the prototype catalytic cracking burner was successfully developed, we delivered the modified catalytic cracking vaporizer to the Army Natick RD&E Center. At the Natick RD&E, Mr. Don Pickard and his technical staff successfully operated catalytic cracking on a variety of fuels. The catalytic cracking burner successfully operated with blue flame on all types of fuels. These fuels included:

- Exxon No. 2 diesel fuel (0.025 % sulfur);
- Army No. 2 diesel fuel (maximum 0.5 % sulfur);
- JP-8; and
- Gasoline.

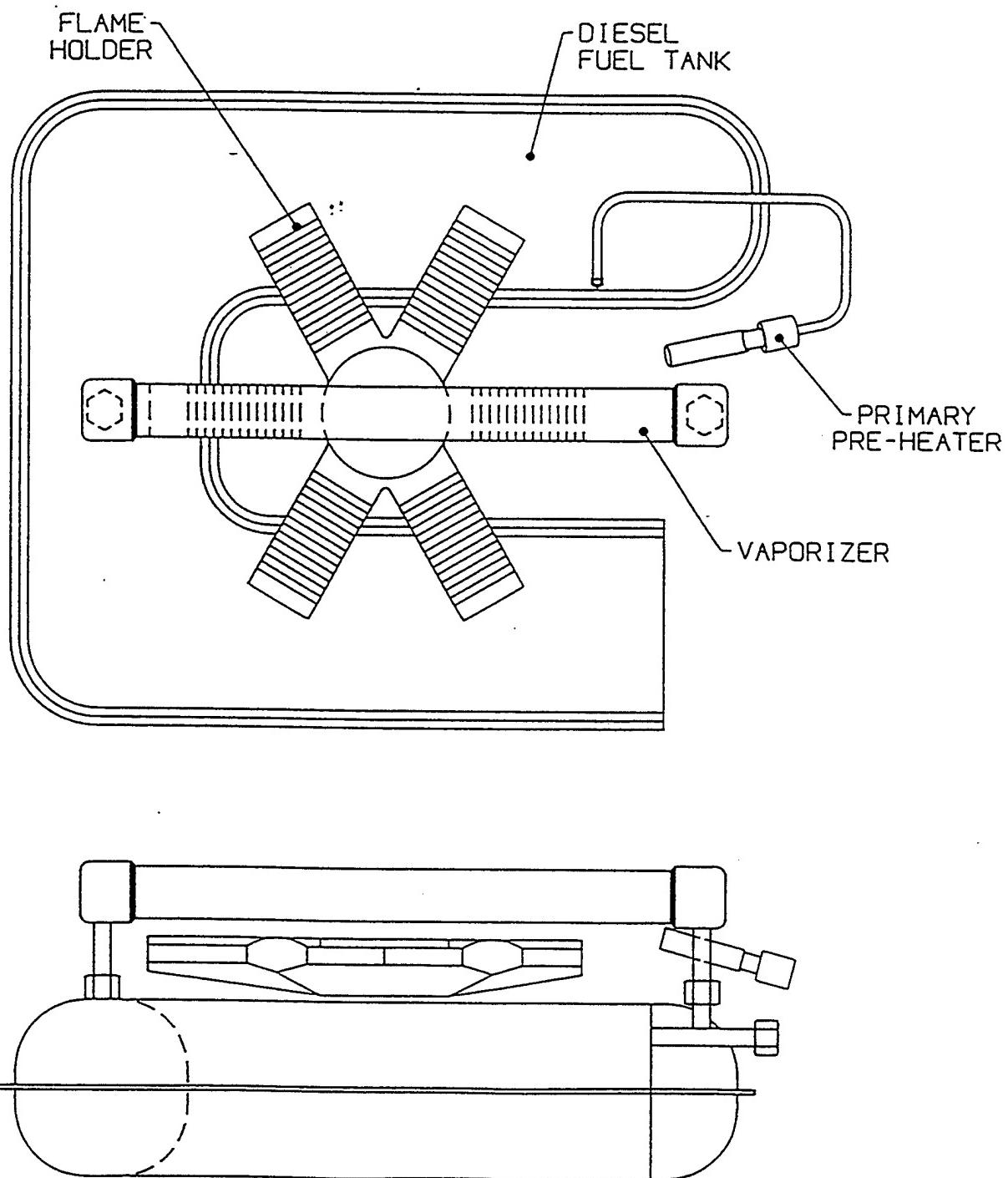


Figure 12: Schematic of the M-3 Burner Preheater Configuration Mounted on the Modified M-2 Burner Catalytic Cracking Unit

4. Conclusions

During Phase II, Aspen Systems, Inc. successfully demonstrated the durability and reliability of the catalytic cracking technology by operating a prototype catalytic cracking burner on diesel for 300 hours. Clean combustion of diesel and wide ranges of firing rate were clearly demonstrated during the entire 300 hour test. There was no sign of coking and sulfur poisoning in the catalysts (which consumed about 970 lbs. of diesel fuel). Sulfur was detected only in an insignificant portion of the catalysts. This result indicated that fuel-bound sulfur was not accumulating in the catalysts as solid, liquid, or any other reaction by-products.

In addition, Aspen successfully produced a working prototype catalytic cracking burner unit by slightly modifying an existing M-2 burner unit. For the prototype burner fabrication, we developed many types of the catalytic cracking vaporizers utilizing nickel coated copper tubings. The new design allowed for a preheating time of less than 5 minutes. Two catalytic cracking vaporizers were fabricated and delivered to Army Natick RD&E Center for performance evaluation. Multifuel capability of the catalytic cracking burner system was successfully demonstrated by operating the burner on Exxon No. 2 diesel (0.025% sulfur), Army No. 2 diesel (maximum 0.5% sulfur), JP-8, and gasoline.

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References

1. Chen, N.Y.; Garwood, W.E.; and Dwyer, F.G., **Shape Selective Catalysis in Industrial Applications**, Marcel Dekker, New York (1989).
2. Moyse, Brian M. and Ward, John W., "Catalyst Selection for Hydrotreater Turnaround," **Oil & Gas Journal** (February 1988).
3. Oblad, A.G.; Milliken, Jr., T.H.; and Mills, G.A., "Chemical Properties of Cracking Catalysts," **Adv. in Catalysis**, Vol. III, P. 240 (1951).
4. Shankland, R.V., "Industrial Catalytic Cracking," **Adv. in Catalysis**, Vol. III, P. 320 (1954).
5. Free, G. and Füner, W.v. German Patent No. 767817, October 13, 1953, **Chem. Abstr.**, Vol. 49(4), P. 111 (1968).
6. Gallagher, J.P.; Humes, W.H.; and Siemssen, J.O., **Chem. Eng. Prog.**, Vol. 75(6), P. 56 (1979).
7. Berber, J.S. and Little, Jr., L.R., **Prepr. Am. Chem. Soc., Div. Fuel Chem.**, P. 86 (1962).
8. Given, P.H., **J. Appl. Chem.**, Vol. 7, P. 172 (1957).
9. O'Hara, J.B, Chow, T.K.,and J.K. Ling, "Hydrogen Production from Liquid Hydrocarbons -Demonstration Program," Final Technical Report: Air Force Program, 63723F/3139, Under MIPR, DAAK70-85-C-0092 (1986).
10. Steinfeld, G., Skaaranderup-Larsen, J., and J. Kahle, "Diesel Fuel Processing for the PAFC Process Demonstration," Final Technical Report: Air Force Program, 63723f/3139, under MIPR, DAAK70-85-c-0090 (1986).
11. Houseman, J. and D.J. Cerini, "Onboard Hydrogen Generation for Automobiles", **11th IECEC, 769001**, P.6, (1976).
12. J. Ryu, et. al., "Catalytic Cracking of Diesel Fuel for Army Field Burners", Final Report, U.S. Army Natick RD&E Center, Contract No. DAAK60-94-C-0030 (1994).